

# WASTES IN PRODUCTION

UDC 666.127:662.998

## HEAT-INSULATING MATERIAL BASED ON CULLET SUBJECTED TO MECHANOCHEMICAL ACTIVATION

A. V. Gorokhovskii,<sup>1</sup> D. V. Meshcheryakov,<sup>1,4</sup> I. N. Burmistrov,<sup>1</sup> D. S. Spiricheva,<sup>1</sup>  
J. I. Escalante-Garcia,<sup>2</sup> and F. Puertas<sup>3</sup>

Translated from *Steklo i Keramika*, No. 1, pp. 6–9, January, 2010.

Methods for recycling mixed cullet, which is a constituent of solid common wastes, are analyzed. It is shown that the problem of recycling wastes of this form remains topical. It is established experimentally that the method of mechanochemical activation makes it possible to obtain a mixed alkaline binding substance which is promising for the production of unfired heat-insulating materials with high mechanical properties.

**Key words:** cullet, mechanochemical activation, heat-insulating materials.

Rational recycling of industrial wastes is inextricably coupled with technical – economic questions concerning resource and energy conservation as well as ecological aspects of environmental protection. The amount of solid domestic wastes (SDW) and industrial wastes is growing steadily throughout the world; their flows are quite strictly monitored, making it possible to prevent mixing and to preserve the possibility of their further use. However, the SDW placed in the reprocessing (storage) sites are in a mixed form. The amount of SDW reaches  $5 \times 10^6$  tons/year in large megalopolises and  $(300 - 400) \times 10^3$  tons/year in regional centers with population  $(0.6 - 1.0) \times 10^6$ . In the 1980s – 1990s SDW were processed mainly in incinerators. However, for all its advantages burning SDW contaminates the atmosphere with the products of combustion, among which, because of the low temperatures of the process (1100 – 1250°C), there are substantial quantities of highly toxic substances (dioxins). In addition, the ash obtained as a result of burning SDW is also dangerous, since it contains a high content of heavy metals [1, 2].

In this connection plants reprocessing SDW by sorting and individual recycling of definite types of wastes (glass, ceramics, and stones, nonferrous metals, ferrous metals,

polymer materials, organic wastes, and paper) are widespread. However, if the problem of reprocessing organic wastes (obtaining biogas and organic fertilizers), polymers (obtaining mixed powders of polymers and their use), as well as metals (smelting in foundries) has been solved, it remains topical for glass and ceramics. According to statistical data, wastes in the form of cullet comprise 2 to 6% of SDW in the European countries while in Russia the SDW contain 6 – 10% glass. Such mixed wastes of glass materials take up large areas at repositories and do not decompose with time because of their high chemical stability [3].

Mixed wastes of glass and glass articles in SDW (sheet glass, glassware, container glass, glass building blocks, mirrors, chemical laboratory and medical glass, ceiling-light shades, and so forth) cannot be used as a raw material in the glass industry because they have different colors and their chemical composition varies over a wide range. In addition, glass wastes have metal-oxide (solar-protective and heat-reflecting glass sheets) and metallic (mirror scraps) as well as polymer (glass containers, ceiling-light shades) coatings which impede their direct recycling in the glass industry.

According to US Environmental Protection Agency data, 77% of all glass and glass articles produced by the glass industry is placed in dumps. In Spain only 56% of the industrial and 27% of domestic glass wastes with a total volume of about  $1 \times 10^6$  tons were reprocessed. The enormous amount of waste glass which is not reprocessed (recycled) encour-

<sup>1</sup> Saratov State Technical University, Saratov, Russia.

<sup>2</sup> CINVESTAV, Saltillo, Mexico.

<sup>3</sup> IETCC, Madrid, Spain.

<sup>4</sup> E-mail: mdv1955@yandex.ru.

rages the search for new technologies which would make it possible to use mixed glass wastes as raw materials for the production of various materials and articles.

Practically all known methods of recycling mixed cullet involve successive operations of crushing and dry grinding, which are easily setup directly at the refuse processing plant.

The product obtained by crushing glass wastes (1–8 mm fragments) can be used as filler in concretes, but there are no advantages over conventional natural fillers. All other known technologies for reprocessing mixed glass wastes employ fine and superfine powders obtained by dry grinding of the products obtained by crushing. Specifically [4–6], it is proposed that they be used for the following:

- puzzolana additives to Portland cement;
- polymer-material fill as well as road coatings and roofing materials;
- component of initial-material mixes for manufacturing composite materials (together with ash, slags, ceramic scrap) fired at temperatures 850–1100°C;
- principal component in the production of foam glass, used together with the foaming agent; the mixtures are fired as 630–850°C;
- raw material for the synthesis of solid sodium silicates or reagent-pure silica.

Nonetheless, all of the foregoing applications of the wastes involve definite technological, economic, and ecological problems and often government obstacles. On the one hand the growth of the construction industry has sharpened the problem of the shortage of inorganic binders, while on the other hand the production of Portland cement entails intense contamination of the atmosphere by carbon dioxide gas, which does not comport with the modern trends in industrial development.

At the same time processes for obtaining inorganic binders that can be used as alternatives to Portland cement with chemical activation of amorphous silicate and aluminosilicates are known [7–9]. The initial materials are various industrial wastes (ash, slags) as well as amorphized clay (metakaolinite) and amorphous rock. The materials obtained by solidifying chemically activated aluminosilicates have high mechanical strength and maintain it when heated to quite high temperatures and in the presence of moisture.

It is also well known that the introduction at room temperature of aluminum powders into colloids, obtained during chemical activation, results in the formation of porous, quite rapidly solidifying materials possessing high mechanical strength and good heat-insulation properties [10]. Pores are formed as a result of hydrogen release during the interaction with a water alkali solution. In this case it is important to obtain heat-insulation material without expensive high-temperature processing — the main drawback of the conventional technology for fabricating foam glass.

In this connection chemical activation is of great interest for obtaining inorganic binders based on mixed glass wastes. However, it should be noted that the overwhelming majority of commercial silicate glasses comprising most household

and industrial wastes contains the following (%<sup>5</sup>): 65–75 SiO<sub>2</sub>, 6–12 CaO, 12–15 Na<sub>2</sub>O as well as some MgO, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub> (in a number of cases PbO and B<sub>2</sub>O<sub>3</sub>) and coloring additives (Ni<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, Se, Mn<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>). The chemical composition of these glasses is chosen so as to impart high chemical stability to them. As a result chemical activation of glass powders with commercial compositions in alkali solutions is impeded. A quite high rate of dissolution is observed only during activation in autoclaves at high pressures with heating. However, this increases the cost of the final product considerably.

On the other hand it is known that wet grinding of silicate glasses is much more efficient than dry grinding, which is widely used for preparing slips for enameling and glazing. Mechanical activation increases the rate of chemical processes in mixtures subjected to grinding, so that a considerable increase of the rate of dissolution of commercial glasses in alkali solutions is to be expected — mechanochemical activation. In addition, the kinetics of dissolution of silicate glasses with commercial compositions under conditions of grinding in combination with concentrated alkali solutions has still not been studied.

In addition, large amount of alkali-containing wastes are in liquid and solid state. In Russia liquid wastes with high contents of alkali are accumulating at rates to  $1 \times 10^6$  m<sup>3</sup>/yr and similar solid wastes to 150,000 tons/yr, and no more than 50% of these wastes are recycled [11]. Of special interest are wastes with a low content of secondary impurities; specifically, suspensions formed when residues of scorched earth are washed from metal castings in concentrated alkali solutions and melts.

It can be supposed that mechanochemical activation of multi-ton quantities of domestic and industrial glass wastes will make it possible to organize the production of inexpensive unfired heat-insulating materials. It is also important that in contrast to known technical solutions the technology being developed can be easily realized for relatively small production facilities created directly on the grounds of refuse-processing plants.

To solve the problem posed a prescription was developed on the basis of a study of the physical-chemical aspects of mechanochemical activation and solidification of mixed domestic and industrial wastes, and a technology was developed for preparing the working mixture in the production of heat-insulating material.

The experiments were performed using a mixture of different types of cullet (%): 30 sheet glass, 30 colorless container glass, 15 green container glass, 15 brown container glass, and 10 glassware. The content of different forms of cullet in the mixture investigated was chosen as the statistical average for Spain and Russia.

After grinding the mixed cullet (standard sample 250 g) was dry-ground for 4 h in a ceramic ball mill with steel balls. The dispersity of the ground product was determined from

<sup>5</sup> Here and below — content by weight.

TABLE 1.

Sample	Content, wt. %					
	glass powder	NaOH	Na <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	glass powder (filler)*	aluminum (foaming agent)*
1	41	6	10	43	41	1.70
2	41	6	10	43	64	1.20
3	41	6	10	43	64	0.30
4	44	6	10	40	70	0.15
5	50	6	10	34	70	0.08

\* Above 100%.

the sifting curve of partial residues of the fractional composition (Fig. 1). The glass powder obtained with average particle size 35  $\mu\text{m}$  was divided into two parts. The first part (100 g) was subjected to mechanochemical activation, while the second part (150 g) was used as a filler in the activated mixture.

Mechanochemical activation was performed in the same ball mill by wet grinding the first part of the glass powder to which different amounts of a mixture of NaOH and Na<sub>2</sub>CO<sub>3</sub> and water were added. The Na<sub>2</sub>CO<sub>3</sub> : NaOH ratio was 1.43 in all experiments and was chosen in accordance with the data presented in the monograph [3], as an example of a mixture whose alkaline solution possesses the highest reactivity with respect to silicate glass.

Next, a pre-prepared second part of the mixture, obtained by primary dry milling of glass powder and aluminum powder and used as a foaming additive, was introduced into the suspension. As the components of the mixture were mixed, gas (H<sub>2</sub>) was released and the paste hardened. A structure possessing open porosity and not settling with time was formed. Complete solidification in room-temperature air of the articles obtained occurred in 36 h. However, solidification in a dessicator at 60°C occurred much sooner.

The composition of the mixtures as well as the properties and structure of the materials obtained are presented in Tables 1 and 2 and in Fig. 2.

Structure formation in the articles based on composition 1 was accompanied by intense gas release followed by the collapse of the foam, which resulted in separation and non-uniform porosity (see Fig. 2). To eliminate this drawback, the

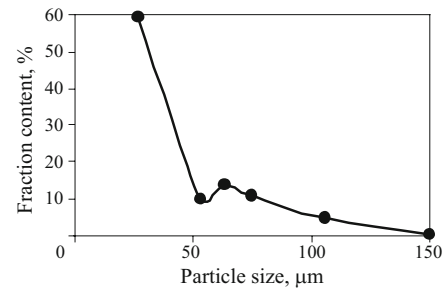


Fig. 1. Fractional composition of glass powder after dry milling.

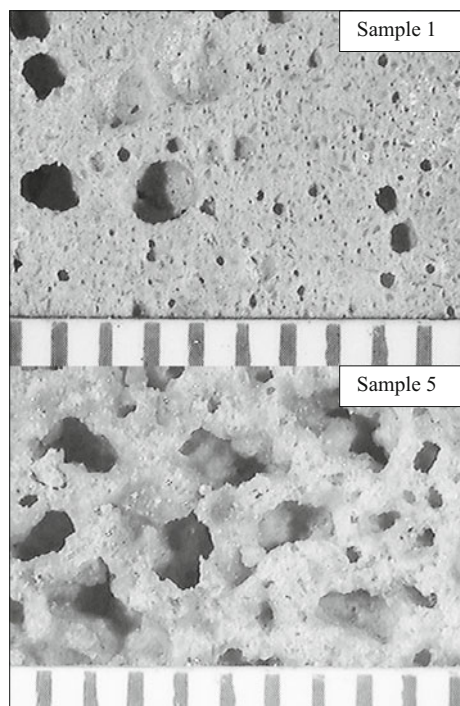
content of the foaming agent (aluminum) was successively decreased in mixtures 2 and 3 with increasing fraction of the milled cullet powder (filler) in the mixture. It was found that as the amount of the added foaming agent decreases, its foaming efficiency increases and at the same time the porosity of the samples of the solidified material increases (from 43 to 60%) and the density of the material decreases (from 1.42 to 1.00 g/cm<sup>3</sup> for composition 3). However, the solidification time of the mixture based on the composition 3 was at least 10 h, even with soaking at 60°C. For this reason, subsequently, the amount of foaming agent added was decreased further with the water-solid ratio decreased at the same time. As a result the solidification time for the mixture based on the composition 5 was decreased to 4 h (60°C).

The porous structure of the material obtained became more uniform with pore sizes ranging from 0.5 to 1.0 mm (see Fig. 2). The physical-mechanical characteristics of the material synthesized on the basis of composition 5 correspond to heat-insulating construction materials. Therefore this material can be recommended for use in the form of elements of thermally stable, rigid, heat insulation for thermal and other engineering systems as well as buildings and structures.

It is useful to dwell on the mechanism of solidification of the suspensions of milled cullet which are subjected to mechanochemical activation. The hydrophilic finely dispersed particles of glass, which are obtained by means of dry milling, possess excess surface energy. When such particles, containing many submicron cracks, come into contact with an alkaline solution during wet milling they undergo intense decomposition to nano sizes, which is accompanied by intense hydrolysis of the surface.

TABLE 2.

Indicator	Sample				
	1	2	3	4	5
Average density, g/cm <sup>3</sup>	1.42 $\pm$ 0.12	1.1 $\pm$ 0.2	1.0 $\pm$ 0.1	1.2 $\pm$ 0.13	1.0 $\pm$ 0.12
Porosity, %	43	56	60	52	60
Thermal conductivity, W/(m · K)	0.41	0.28	0.22	0.34	0.24
Compression strength, MPa (after 7 days)	—	8.3 $\pm$ 0.4	4.5 $\pm$ 0.3	—	5.6 $\pm$ 0.5



**Fig. 2.** Structure of the obtained heat-insulating materials (ruler scale 1 mm/division).

The surface silanol groups formed possess amphoteric properties [12], as a result of which the ultradispersed amorphous particles of glass undergo polycondensation and colloidization and the system obtained solidifies. To no small extent this is due to the fact that when most of the glass powder is dissolved in an alkaline solution a proportional amount of CaO and MgO, which act as solidifying agents for the alkali-silicate colloid, pass into the solution. Thus, in the case of mixture 5, which permits obtaining material with optimal usage properties, 70% of the mass of the glass powder dissolved in the course of mechanochemical activation, and the colloidal solution formed in the process contains (%): 53.9 SiO<sub>2</sub>, 37.0 Na<sub>2</sub>O, 7.4 CaO, and 1.7 MgO.

*This work was supported by RFFI (joint RFFI–INIS committee, project 09-08-91270).*

## REFERENCES

1. A. A. Dreier, A. N. Sachkov, and K. S. Nikol'skii, *Solid Industrial and Household Wastes, Their Properties and Processing* [in Russian], Khimiya, Moscow (1997).
2. L. A. Fedorov, *Dioxins as an Ecological Hazard: Retrospective and Prospects* [in Russian], Nauka, Moscow (1993).
3. M. A. Bezborodov, *Chemical Stability of Silicate Glasses* [in Russian], Nauka i Tekhnika, Minsk (1972).
4. L. Barbieri, A. M. Ferrari, I. Lancellotti, and C. Leonelli, "Crystallization of (Na<sub>2</sub>O – MgO) – CaO – Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> glass systems formulated from waste products," *J. Amer. Ceram. Soc.*, **83**(10), 2515 – 2520 (2000).
5. Yu. A. Spridonov and L. A. Orlova, "Problems of obtaining foam glass," *Steklo Keram.*, No. 10, 10 – 11 (2003).
6. N. Mori, "Extraction of silicon dioxide from waste glasses and their recycling process," in: *20th International Congress on Glass*, Kyoto (2004), pp. 05.006/1 – 05.006/5.
7. A. Buchwald and M. Schulz, "Alkali-activated binders by use of industrial by-products," *Cement Concr. Res.*, **35**, 968 – 973 (2004).
8. A. Fernandez, J. G. Palomo, and F. Puertas, "Alkali-activated slag mortars mechanical strength behavior," *Cement Concr. Res.*, **29**, 1312 – 1321 (1999).
9. J. I. Escalante-Garcia, K. Campos-Venegas, and A. Gorokhosky, "Cementitious composites of pulverized fuel ash and blast furnace slag activated by sodium silicate: effect of Na<sub>2</sub>O concentration and modulus," *Adv. Appl. Ceram.*, **105**(4), 201 – 208 (2006).
10. A. A. Shishkin and N. V. Astakhova, *Activated Binding Substances and Concretes Based on Them* [in Russian], Stroiizdat, Moscow (2001).
11. N. I. Min'ko and V. I. Onishchuk, "Use of secondary alkali-containing initial materials in the glass industry," *Steklo Keram.*, No. 2, 2 – 3 (1990).
12. A. V. Gorokhovskii, "On the nature of acidic centers of the surface of window-type commercial silicate glasses," *Fiz. Khim. Stekla*, **14**(5), 739 – 743 (1988).